10/16/00 A

Express Mail Label No. EL598673427US

UTILITY PATENT APPLICATION TRANSMITTAL
(Large Entity)

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Docket No.
END-00-0034US1

Total Pages in this Submission
4

TO THE ASSISTANT COMMISSIONER FOR PATENTS
Box Patent Application
Washington, D.C. 20231

Transmitted herewith for filing under 35 U.S.C. 111(a) and 37 C.F.R. 1.53(b) is a new utility patent application for an invention entitled:

SOLDER PROTECTIVE COATING AND FLUXLESS JOINING OF FLIP CHIP DEVICES ON LAMINATES WITH PLATED SOLDER

and invented by:

W. E. Bernier et al.

If a CONTINUATION APPLICATION, *check appropriate box and supply the requisite information:*

☐ **Continuation** ☐ **Divisional** ☐ **Continuation-in-part (CIP)** of prior application No.: _____

Which is a:

☐ **Continuation** ☐ **Divisional** ☐ **Continuation-in-part (CIP)** of prior application No.: _____

Which is a:

☐ **Continuation** ☐ **Divisional** ☐ **Continuation-in-part (CIP)** of prior application No.: _____

Enclosed are:

Application Elements

1. ☒ Filing fee as calculated and transmitted as described below

2. ☒ Specification having **11** pages and including the following:

   a. ☒ Descriptive Title of the Invention

   b. ☐ Cross References to Related Applications *(if applicable)*

   c. ☐ Statement Regarding Federally-sponsored Research/Development *(if applicable)*

   d. ☐ Reference to Microfiche Appendix *(if applicable)*

   e. ☒ Background of the Invention

   f. ☒ Brief Summary of the Invention

   g. ☒ Brief Description of the Drawings *(if drawings filed)*

   h. ☒ Detailed Description

   i. ☒ Claim(s) as Classified Below

   j. ☒ Abstract of the Disclosure

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Application Elements (Continued)

3. ☒ Drawing(s) *(when necessary as prescribed by 35 USC 113)*
   a. ☐ Formal 1 SHEET Number of Sheets _____
   b. ☐ Informal Number of Sheets _____

4. ☒ Oath or Declaration
   a. ☒ Newly executed *(original or copy)* ☐ Unexecuted
   b. ☐ Copy from a prior application (37 CFR 1.63(d)) *(for continuation/divisional application only)*
   c. ☒ With Power of Attorney ☐ Without Power of Attorney
   d. ☐ *DELETION OF INVENTOR(S)*
      Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. 1.63(d)(2) and 1.33(b).

5. ☐ Incorporation By Reference *(usable if Box 4b is checked)*
   The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.

6. ☐ Computer Program in Microfiche *(Appendix)*

7. ☐ Nucleotide and/or Amino Acid Sequence Submission *(if applicable, all must be included)*
   a. ☐ Paper Copy
   b. ☐ Computer Readable Copy *(identical to computer copy)*
   c. ☐ Statement Verifying Identical Paper and Computer Readable Copy

Accompanying Application Parts

8. ☒ Assignment Papers *(cover sheet & document(s))*

9. ☐ 37 CFR 3.73(B) Statement *(when there is an assignee)*

10. ☐ English Translation Document *(if applicable)*

11. ☒ Information Disclosure Statement/PTO-1449 ☒ Copies of IDS Citations

12. ☐ Preliminary Amendment

13. ☒ Acknowledgment postcard

14. ☒ Certificate of Mailing
    ☐ First Class ☒ Express Mail *(Specify Label No.):* **EL598673427US**

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Accompanying Application Parts (Continued)

15. ☐ Certified Copy of Priority Document(s) *(if foreign priority is claimed)*

16. ☐ Additional Enclosures *(please identify below):*

Request That Application Not Be Published Pursuant To 35 U.S.C. 122(b)(2)

17. ☐ Pursuant to 35 U.S.C. 122(b)(2), Applicant hereby requests that this patent application not be published pursuant to 35 U.S.C. 122(b)(1). Applicant hereby certifies that the invention disclosed in this application has not and will not be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication of applications 18 months after filing of the application.

Warning

An applicant who makes a request not to publish, but who subsequently files in a foreign country or under a multilateral international agreement specified in 35 U.S.C. 122(b)(2)(B)(i), must notify the Director of such filing not later than 45 days after the date of the filing of such foreign or international application. A failure of the applicant to provide such notice within the prescribed period shall result in the application being regarded as abandoned, unless it is shown to the satisfaction of the Director that the delay in submitting the notice was unintentional.

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Fee Calculation and Transmittal

CLAIMS AS FILED

For	#Filed	#Allowed	#Extra		Rate	Fee
Total Claims	32	- 20 =	12	x	$18.00	$216.00
Indep. Claims	2	- 3 =	0	x	$80.00	$0.00
Multiple Dependent Claims (check if applicable) ☐						$0.00
					BASIC FEE	$710.00
OTHER FEE *(specify purpose)* _____						$0.00
					TOTAL FILING FEE	$926.00

☐ A check in the amount of to cover the filing fee is enclosed.

☒ The Commissioner is hereby authorized to charge and credit Deposit Account No. **09-0457** as described below. A duplicate copy of this sheet is enclosed.

- ☒ Charge the amount of **$926.00** as filing fee.
- ☒ Credit any overpayment.
- ☒ Charge any additional filing fees required under 37 C.F.R. 1.16 and 1.17.
- ☐ Charge the issue fee set in 37 C.F.R. 1.18 at the mailing of the Notice of Allowance, pursuant to 37 C.F.R. 1.311(b).

Dated: October 11, 2000

Signature

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cc: **RECORDS**

APPLICATION

FOR

UNITED STATES LETTERS PATENT

APPLICANT NAME: William E. Bernier
Donald W. Henderson
James Spalik
Isabelle Paquin

TITLE: SOLDER PROTECTIVE COATING AND FLUXLESS JOINING OF FLIP CHIP DEVICES ON LAMINATES WITH PLATED SOLDER

DOCKET NO: 0135/00311

INTERNATIONAL BUSINESS MACHINES CORPORATION

CERTIFICATE OF MAILING UNDER 37 CFR § 1.10
IBM Docket No. END-00-0034US1

I hereby certify that, on the date shown below, this correspondence is being deposited with the United States Postal Service in an envelope addressed to the Commissioner for Patents, Washington, D.C. 20231 as "Express Mail Post Office to Addressee"
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Name of person mailing paper

June M. Mitchell 10/12/00
Signature Date

SOLDER PROTECTIVE COATING AND FLUXLESS JOINING OF FLIP CHIP DEVICES ON LAMINATES WITH PLATED SOLDER

William E. Bernier, Donald W. Henderson, James Spalik and Isabelle Paquin

FIELD OF THE INVENTION

The invention relates to the fluxless joining of flip chip devices on laminates with plated solder. The invention also relates to the protection of such solder joinable surfaces against excess oxidation.

BACKGROUND OF THE INVENTION

Fluxes are commonly reacted with surface oxides, such as tin oxide, during the reflow process to generate metal surfaces which subsequently intermix forming a solder joint. Problems in fluxing and soldering can arise in which inadequate amounts of flux or excessive thicknesses of tin oxide are present either or both of which can inhibit wetting and intermixing and result in the formation of non wetted, electrically open solder joints. In addition, where excess flux may be incompletely consumed in the reflow process. The remaining residues will interfere with the efficiency of subsequent process steps such as chip underfill.

Routinely, tin oxide is controlled by multiple reflows of solder in the presence of flux which subsequently must be removed, either by aqueous, organic solvent, or gaseous cleaning. The newly-cleaned surfaces are now subject to reoxidation by exposure to ambient air, thus the thickness of tin oxide layer may vary unacceptably in an uncontrolled manner.

Currently, a variety of flux types, both those that do not require a separate cleaning step, no clean, and types that are removed by aqueous, or organic solvent washing are employed in the electronics industry. These fluxes introduce residues onto laminate, solder joint and chip surfaces which can inhibit proper underfill flow required for subsequent mechanical stability of the solder joints.

SUMMARY OF THE INVENTION

This invention selectively precoats the solder surfaces of either the chip, the laminate, or both with a metal-complexing agent in a flux which reacts with the tin oxide in order to control the reactivity of tin at the solder surface. This complexing agent forms a continuous thin metal carboxylate film on the solder surfaces and protects the solder surface from further oxide formation. In this form the chips and laminates may be handled in a routine manner without particular concern for oxide thickness growth as long as mechanical damage to the solder surfaces is avoided. When ready for joining the chip solder bumps and laminate solder pads are brought into intimate contact and subjected to reflow temperatures. The tin carboxylate complex facilitates solder reflow, but moreover, when exposed to peak reflow temperatures, decomposes into volatile products, leaving a clean surface easily wetted by the solder.

This invention may be carried out applying additional flux just prior to reflow, or the additional flux application may be omitted resulting in a fluxless joining process. Where the flux is omitted, the treated chips or laminates, now having protected surfaces, may be safely stored for later final assembly. Advantages of the invention include control of the tin oxide formation prior to chip joining, handling improvement, opportunity for fluxless joining and elimination of residues after reflow promoting underfill adhesion.

The invention provides a method of protecting tin solderable surfaces. To a solderable surface, coated with tin oxide, a complexing agent is applied. The complexing agent is, a dicarboxylic acid, for example, pimelic acid. Heating drives the formation of tin pimelate which forms a tenacious film over the solder surface protecting it from reacting

further with ambient oxygen. The protective agent, tin pimelate in this example, also prevents the oxidation of Sn(II) to Sn(IV). Sn(IV) is well known to be difficult to complex and to inhibit the solder process.

The invention provides a means of generating clean metal surfaces for solder joining without incurring problems associated with the use of customary flux. An aspect of the invention is that the temperatures associated with reflow decompose the protective agent to volatile materials, in the present example, tin pimelate is decomposed to cyclohexanone and CO_2. The decomposition results in a clean surface.

An additional aspect of the invention is provision of means of protection against oxidation of solderable surfaces during storage awaiting final assembly.

Yet a further aspect of the invention is provision of means by which flux contamination of extraneous surfaces is prevented. The present invention eliminates the need for flux, usually required for multiple reflow steps, and minimize the further growth of the tin oxide layer. The present invention substantially eliminates flux residues since the decomposition products are gaseous.

Still other objects and advantages of the present invention will become readily apparent by those skilled in the art from the following detailed description, wherein it is shown and described preferred embodiments of the invention, simply by way of illustration of the best mode contemplated of carrying out the invention. As will be realized the invention is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, without departing from the invention. Accordingly, the description is to be regarded as illustrative in nature and not as restrictive.

SUMMARY OF DRAWINGS

The invention is best understood from the following detailed description when read in connection with the accompanying drawing. It is emphasized that, according to common practice, the various features of the drawing are not to scale. On the contrary, the dimensions of the various features are arbitrarily expanded or reduced for clarity.

Figure 1 is a schematic outlining the steps of the method.

DETAILED DESCRIPTION OF INVENTION

Reference is made to the figures to illustrate selected embodiments and preferred modes of carrying out the invention. It is to be understood that the invention is not hereby limited to those aspects depicted in the figure.

In **Step A**, a first tin solderable surface **1** and a second tin solderable surface **5**, each of the surfaces having a natural film of tin oxide **2** thereon, are provided. In **Step B**, a complexing agent **3** is applied. In some embodiments of the invention, the complexing agent is pimelic acid applied from a vapor phase. The complexing agent forms an addition product **4** with the oxide coating, in some embodiments, a cyclic tin pimelate product. In some embodiments of the invention, the parts, with solder joinable surfaces protected by the addition product, are stored for later final assembly. **Step C** intimately contacts the first and second surfaces. In **Step D**, reflow conditions are applied, forming a solder joint, decomposing the addition product to volatile materials **6**.

In those embodiments wherein the complexing agent is applied from the gas phase, without using flux, the parts may be stored for later assembly. Such gas phase embodiments are considered examples of the best mode of employing the invention. In such embodiments, the complexing agent may be a dicarboxylic acid that decomposes to volatile products when exposed to solder reflow conditions. Non-limiting examples of suitable dicarboxylic acids include adipic acid, pimelic acid, sebacic acid, and other dibasic acids.

According to certain embodiments of the invention, the first tin-solderable surface is a chip solder bump surface and the second tin-solderable surface is a laminate solder pad.

In some embodiments of the invention, the complexing agent comprises EN92 flux as described in U.S. Patents 5,615,827 and 5,531,838 assigned to the assignee of the present invention the disclosure of which is hereby incorporated by reference. In such embodiments, the treated parts are not stored, but reflow occurs substantially immediately after application of complexing agent. In other embodiments wherein reflow occurs

substantially immediately after application of complexing agent, the complexing agent may comprise a mixture comprising suitable flux and any of adipic acid, pimelic acid, sebacic acid, or any other dicarboxylic or dibasic acid that decomposes to volatile products when exposed to reflow conditions. Reflow conditions comprise temperatures of about 220° C. Appropriate amounts of flux and complexing agents are as described in the above referenced patents.

It will, therefore, be appreciated by those skilled in the art having the benefit of this disclosure that this invention is capable of producing various tin carboxylate coatings on tin-solderable surfaces. It will be further appreciated that such coatings provide protection against further oxidation of such treated surfaces. Moreover, it will be appreciated that such surfaces are in a state suitable for solder joining under reflow conditions. Furthermore, it is to be understood that the form of the invention shown and described is to be taken as presently preferred embodiments. Various modifications and changes may be made to each and every processing step as would be obvious to a person skilled in the art having the benefit of this disclosure. It is intended that the following claims be interpreted to embrace all such modifications and changes and, accordingly, the specification and drawings are to be regarded in an illustrative rather than a restrictive sense.

CLAIMS

What is claimed is:

1. A method of protecting tin solderable surfaces comprising:

providing a solderable surface having tin oxide thereon;

applying complexing agent to said solderable surface; and

forming reaction product with said tin oxide and said complexing agent, wherein said reaction product decomposes to tin oxide and volatile products upon being exposed to reflow conditions.

2. A method of protecting tin solderable surfaces, according to claim 1, wherein said complexing agent forms a reaction product with tin.

3. A method of protecting tin solderable surfaces, according to claim 1, wherein said complexing agent and tin react to form a tin carboxlyate.

4. A method of protecting tin solderable surfaces, according to claim 1, wherein forming said reaction product with said tin oxide and said complexing agent comprises heating.

5. A method of protecting tin solderable surfaces, according to claim 1, wherein said reaction product decomposes to volatile products where subject to reflow temperatures.

6. A method of protecting tin solderable surfaces, according to claim 1, wherein said complexing agent comprises pimelic acid.

7. A method of protecting tin solderable surfaces, according to claim 1, wherein said complexing agent further comprises flux.

8. A method of protecting tin solderable surfaces, according to claim 1, wherein said complexing agent comprises sebacic acid.

9. A method of protecting tin solderable surfaces, according to claim 1, wherein said complexing agent is selected from the group consisting of dicarboxylic acids, dibasic acids, and complexing agents.

10. A method of protecting tin solderable surfaces, according to claim 1, wherein said reaction product comprises tin pimelate.

11. A method of protecting tin solderable surfaces, according to claim 1, wherein said reaction product comprises tin dicarboxylate.

12. A method of joining tin-solderable surfaces comprising:

providing a first tin solderable surface and a second tin solderable surface, each said surface having tin oxide thereon;

applying complexing agent to said at least one tin solderable surface;

forming reaction product with said tin oxide and said complexing agent, wherein said reaction product decomposes to tin oxide and volatile products upon being exposed to reflow conditions;

intimately contacting a first tin solderable surface with a second tin solderable surface; and

reflowing said first and said second surfaces.

13. A method of joining tin-solderable surfaces, according to claim 12, wherein said first tin solderable surface is a chip solder bump surface; and wherein said second tin solderable surface; is a laminate solder pad.

14. A method of joining tin-solderable surfaces, according to claim 12, wherein said complexing agent forms a reaction product with tin.

15. A method of joining tin-solderable surfaces, according to claim 12, wherein forming said reaction product with said tin oxide and said complexing agent comprises heating.

16. A method of joining tin-solderable surfaces, according to claim 12, wherein said complexing agent comprises pimelic acid.

17. A method of joining tin-solderable surfaces, according to claim 12, wherein said complexing agent further comprises flux.

18. A method of joining tin-solderable surfaces, according to claim 12, wherein said complexing agent is a dicarboxylic acid.

19. A method of joining tin-solderable surfaces, according to claim 12, wherein said reaction product comprises tin pimelate.

20. A method of joining tin-solderable surfaces, according to claim 12, wherein said reaction product comprises tin dicarboxylate.

21. A method of joining tin-solderable surfaces, according to claim 12, wherein said reaction product decomposes to volatile products where subject to reflow temperatures.

22. A method of joining tin-solderable surfaces, according to claim 12, wherein said complexing agent and tin react to form tin carboxlyate.

23. A method of protecting tin solderable surfaces, according to claim 1, wherein applying complexing agent comprises vapor phase deposition of complexing agent.

24. A method of protecting tin solderable surfaces, according to claim 1, wherein complexing agent comprises adipic acid.

25. A method of protecting tin solderable surfaces, according to claim 12, wherein forming said reaction product with said tin oxide and said complexing agent comprises heating.

26. A method of joining tin-solderable surfaces, according to claim 12, wherein applying complexing agent comprises vapor phase deposition of complexing agent.

27. A method of protecting tin solderable surfaces, according to claim 12, wherein said complexing agent comprises sebacic acid.

28. A method of protecting tin solderable surfaces, according to claim 12, wherein complexing agent comprises adipic acid.

29. The structure containing reaction product according to claim 1.

30. The structure containing at least one solder joint formed according to claim 1.

31. The structure containing reaction product according to claim 12.

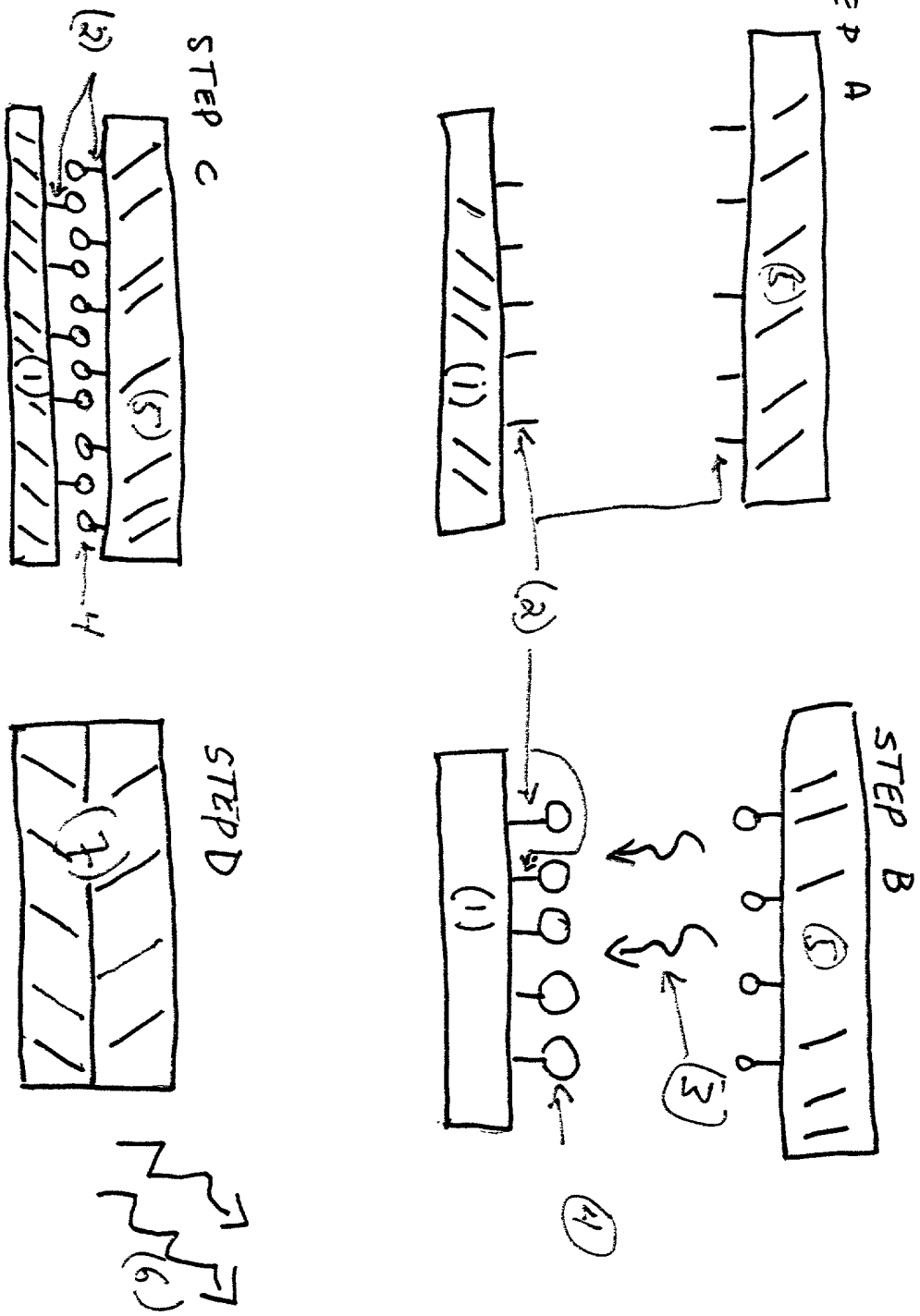
32. The structure containing at least one solder joint formed according to claim 12.

SOLDER PROTECTIVE COATING AND FLUXLESS JOINING OF FLIP CHIP DEVICES ON LAMINATES WITH PLATED SOLDER

ABSTRACT

A method for protecting tin oxide coated solder surfaces against further oxidation and a method for fluxless solder joining of such surfaces is provided.

Fig 1



DECLARATION FOR PATENT APPLICATION

English Language Declaration

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

SOLDER PROTECTIVE COATING AND FLUXLESS JOINING OF FLIP CHIP DEVICES ON LAMINATES WITH PLATED SOLDER

☐ the specification of which
☑ (check one)

☒ is attached hereto.
☐ was filed on _____, as United States Patent Application Serial No. or PCT International Application Number _____, and was amended on _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with 37 CFR § 1.56(a).

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate listed below, or § 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

			Priority Claimed	
_____	_____	_____	[ ]	[ ]
(Application No.)	(Country)	(Day/Month/Year Filed)	YES	NO
_____	_____	_____	[ ]	[ ]
(Application No.)	(Country)	(Day/Month/Year Filed)	YES	NO
_____	_____	_____	[ ]	[ ]
(Application No.)	(Country)	(Day/Month/Year Filed)	YES	NO

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below:

(Application Serial No.)	(Filing Date)
(Application Serial No.)	(Filing Date)
(Application Serial No.)	(Filing Date)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by 35 U.S.C. § 112, first paragraph, I acknowledge the duty to disclose material information as defined in 37 CFR § 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(U.S. Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(U.S. Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(U.S. Filing Date)	(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (*list name and registraton number*)

David L. Adour, Reg. No. 29,604, Lawrence R. Fraley, Reg. No. 26,885, John R. Pivnichny, Reg. No. 43,001, Arthur J. Samodovitz, Reg. No. 31,297, William H. Steinberg, Reg. No. 28,540; all of INTERNATIONAL BUSINESS MACHINES CORPORATION; George Vande Sande, Reg. No. 17,276, Burton A. Amernick, Reg. No. 24,852, Richard Wiener, Reg. No. 18,741, Townsend M. Belser, Jr., Reg. No. 22,956; Morris Liss, Reg. No. 24,510, Martin Abramson, Reg. No. 25,787, George R. Pettit, Reg. No. 27,369, Elzbieta Chlopecka, Reg. No. 32,767, Eric J. Franklin, Reg. No. 37,134, and William E. Curry, Reg. No. 43,572, David W. Ward, Reg. No. 45,198, and John A. Evans, Ph.D., Reg. No. 44,100; all of POLLOCK, VANDE SANDE & AMERNICK; John E. Hoel, Reg. No. 26,279, Christopher A. Hughes, Reg. No. 26,914, Edward A. Pennington, Reg. No. 32,588; Joseph C. Redmond, Jr., Reg. No. 18,753; all of MORGAN & FINNEGAN, L.L.P.

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Inventor's Signature Isabelle Paquin Date 26 septembre 2000

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Full name of fifth joint inventor (if any)

Inventor's Signature Date

Residence Address

Citizenship

Post Office Address

Full name of sixth joint inventor (if any)

Inventor's Signature Date

Residence Address

Citizenship

Post Office Address

Full name of seventh joint inventor (if any)

Inventor's Signature Date

Residence Address

Citizenship

Post Office Address